a) reacting propene with hydrogen peroxide in the presence of a catalyst mixture comprising a phase transfer catalyst, phosphoric acid and a heteropolytungstate in a liquid reaction mixture comprising an aqueous phase with a maximum apparent pH of 6 and an organic phase, herein the term “apparent pH” here refers to a value determined by measurement with a glass electrode employing a commercial pH meter calibrated with aqueous buffer solutions of known pH for measuring dilute aqueous solutions;

b) separating the reaction mixture into an aqueous phase (P_a) comprising 1,2-propanediol and formic acid and an organic phase (P_o);

c) recycling at least a part of the separated organic phase (P_o) to the reaction step a);

d) contacting at least a part of the aqueous phase (P_a) separated in step b) with a palladium catalyst to provide a treated aqueous phase, wherein no hydrogen is added in contacting step d); and

e) recovering 1,2-propanediol from the treated aqueous phase provided in step d).

[007] In a further aspect the present invention relates to the use of a contacting step d) to decompose formic acid in a method for the preparation of 1,2-propanediol comprising:

a) Reacting propene with hydrogen peroxide in the presence of a catalyst mixture comprising a phase transfer catalyst, phosphoric acid and a heteropolytungstate in a liquid reaction mixture comprising an aqueous phase with a maximum apparent pH of 6 and an organic phase, wherein the term “apparent pH” here refers to a value determined by measurement with a glass electrode employing a commercial pH meter calibrated with aqueous buffer solutions of known pH for measuring dilute aqueous solutions;

b) separating the reaction mixture into an aqueous phase (P_a) comprising 1,2-propanediol and formic acid and an organic phase (P_o);

c) recycling at least a part of the separated organic phase (Po) to the reaction step a);

d) contacting at least a part of the aqueous phase (P_a) separated in step b) with a palladium catalyst to provide a treated aqueous phase; and

e) recovering 1,2-propanediol from the treated aqueous phase provided in step d).

Detailed description of the invention

[008] In the method of the present invention, propene is reacted in a step a) with hydrogen peroxide in the presence of a catalyst mixture comprising a phase transfer catalyst and a heteropolytungstate. This reaction is carried out in a liquid reaction mixture which comprises an aqueous phase with a maximum apparent pH of 6 and an organic phase.

[009] Propene can be used in pure form or in a mixture with propane, wherein the proportion of propane may be up to 20 mol-%. The proportion of propane in the propene used is preferably less than 5 mol-%. Propene is preferably employed in a molar excess to hydrogen peroxide, preferably in a molar ratio of propene to hydrogen peroxide of from 1.1:1 to 10:1.

[010] Hydrogen peroxide is preferably used in the form of an aqueous solution, preferably with a hydrogen peroxide content of 10 to 80 % by weight, particularly preferably 30 to 70 % by weight.

Any commercially available grade of aqueous hydrogen peroxide solutions can be used. A crude hydrogen peroxide product obtained in the extraction stage of the anthraquinone process for producing hydrogen peroxide may also be used.

Claims:

1. A method for the preparation of 1,2-propanediol comprising:
   a) reacting propene with hydrogen peroxide in the presence of a catalyst mixture comprising a phase transfer catalyst, phosphoric acid and a heteropolytungstate in a liquid reaction mixture comprising an aqueous phase with a maximum apparent pH of 6 and an organic phase, wherein the term “apparent pH” here refers to a value determined by measurement with a glass electrode employing a commercial pH meter calibrated with aqueous buffer solutions of known pH for measuring dilute aqueous solutions;
   b) separating the reaction mixture into an aqueous phase (P_a) comprising 1,2-propanediol and formic acid and an organic phase (P_o);
   c) recycling at least a part of the separated organic phase (P_o) to the reaction step a);
   d) contacting at least a part of the aqueous phase (P_a) separated in step b) with a palladium catalyst to provide a treated aqueous phase, wherein no hydrogen is added in contacting step d); and
   e) recovering 1,2-propanediol from the treated aqueous phase provided in step d).

2. The method of claim 1, wherein the contacting in step d) is conducted at a pressure sufficient to maintain a liquid aqueous phase.

3. The method of claim 2, wherein the pressure in the contacting step d) is from 1 to 100 bar.

4. The method of any one of claims 1 to 3, wherein the temperature in the contacting step d) is between 0 °C and 200 °C, preferably in the range of 100 °C to 180 °C.

5. The method of any one of claims 1 to 4, wherein between steps b) and d) or between steps d) and e) at least a part of the aqueous phase is subjected to a step f) of catalytic hydrogenation at a temperature in the range of 80 °C to 140 °C, preferably 90 °C to 120 °C.

6. The method of any one of claims 1 to 5, wherein step e) comprises a multi-step distillation, with the first distillation step and optionally further distillation steps providing an overhead product comprising water and a bottoms product which is passed to the next distillation step, and a distillation step providing an overhead product comprising 1,2-propanediol and a residuals bottoms product.

7. The method of claim 6, wherein the residuals bottom product is subjected to at least one further distillation step.

8. The method of any one of claims 1 to 7, wherein phosphoric acid is present in step a) and the heteropolytungstate is a polytungstophosphate.

9. The method of any one of claims 1 to 8, wherein the organic phase in step a) comprises an organic solvent having a boiling point of more than 100 °C at atmospheric pressure and a

solubility in water at 20 °C of less than 250 mg/kg, the organic solvent being preferably selected from alkylated aromatic hydrocarbons having 8 to 12 carbon atoms.

10. The method of any one of claims 1 to 9, wherein the phase transfer catalyst is selected from tertiary amines and tertiary or quaternary ammonium salts and comprises in total at least 12 carbon atoms.

11. The method of claim 10, wherein the phase transfer catalyst comprises a tertiary or quaternary ammonium ion having the structure $R^1R^2R^3NR^4{}^+$, wherein R^1, R^2 and R^3 are the same or different and are each selected from alkyl groups having from 8 to 10 carbon atoms and R^4 is hydrogen or methyl.

12. Use of a contacting step d) to decompose formic acid in a method for the preparation of 1,2-propanediol comprising:

a) reacting propene with hydrogen peroxide in the presence of a catalyst mixture comprising a phase transfer catalyst, phosphoric acid and a heteropolytungstate in a liquid reaction mixture comprising an aqueous phase with a maximum apparent pH of 6 and an organic phase, wherein the term “apparent pH” here refers to a value determined by measurement with a glass electrode employing a commercial pH meter calibrated with aqueous buffer solutions of known pH for measuring dilute aqueous solutions;

b) separating the reaction mixture into an aqueous phase (P_a) comprising 1,2-propanediol and phosphoric acid esters of 1,2-propanediol and an organic phase (P_o);

c) recycling at least a part of the separated organic phase (P_o) to the reaction step a);

d) contacting at least a part of the aqueous phase (P_a) separated in step b) with a palladium catalyst to provide a treated aqueous phase; and

e) recovering 1,2-propanediol from the treated aqueous phase provided in step d).

13. The use of claim 12, wherein the method for the preparation of 1,2-propanediol is performed as defined in any one of claims 2 to 11.